

CLAIMS

Having thus described the invention, what we claim is:

1. An acid copper electroplating composition comprising an aqueous solution of an acid and a copper salt, the improvement comprising the addition of at least one of a carrier compound; a water-soluble, mercapto-containing organic brightener compound; and a leveler compound which comprises an organic compound containing single and multiply charged centers.  
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2. The composition as claimed in claim 1 wherein said acid is sulfuric acid.
3. The composition as claimed in claim 1 wherein said copper salt is selected from the group consisting of copper sulfate, copper acetate, copper fluoborate, cupric nitrate and copper pyrophosphate.
4. The composition as claimed in claim 3 wherein said copper salt is copper sulfate.
5. The composition as claimed in claim 1 wherein said carrier compound is selected from the group consisting of a polysaccharide compound, polyethylene glycol and poly(ethylene oxide).
6. The composition as claimed in claim 1 wherein said polysaccharide carrier is selected from the group consisting of starch, cellulose, amylopectin and amylose.
7. The composition as claimed in claim 1 wherein said water-soluble, mercapto-containing organic brightener is selected from the group consisting of *N*-methylallyl-*N'*-methylthiourea; tetramethylthiuram disulfide; ethylethylthiomethyl sulfoxide; ammonium diethyldithiocarbamate; dimethyl-2-thioxo-1,3-dithiole-4,5-dicarboxylate;  
5 3-mercaptopropanesulfonic acid sodium salt; 3-mercaptopropanesulfonic acid; bis (2-mercaptopropanesulfonic acid); ethylene trithio carbonate; ethanethiol; 2-

mercaptoethanol; monothioglycerol (1-thioglycerol); 1,2-ethanedithiol; and thiодиethanol.

8. The composition as claimed in claim 7 wherein said water-soluble, mercapto-containing organic brightener is selected from the group consisting of ammonium diethyldithiocarbamate, 3-mercaptopropanesulfonic acid sodium salt, and 3-mercaptopropanesulfonic acid.

9. The composition as claimed in claim 1 wherein said leveler is selected from the group consisting of polymeric levelers, low molecular weight levelers and organic dyes.

10. The composition as claimed in claim 9 wherein said polymeric leveler is selected from the group consisting of polyethylenimine, 80% ethoxylated; poly(allylamine); poly(allylamine hydrochloride); polyaniline, sulfonated, 5 wt. % in water, 75 mole % sulfonated; poly[bis(2-chloroethyl)ether-*alt*-1,3-bis[3-(dimethylamino)propyl]urea, quaternized; poly[N,N'-bis(2,2,6,6-tetramethyl-4-piperidinyl)-1,6-hexanediamine-*co*-2,4-dichloro-6-morpholino-1,3,5-triazine; polyacrylamide; poly(acrylamide-*co*-diallyldimethylammonium chloride); poly(diallyldimethylammonium chloride); poly(melamine-*co*-formaldehyde), partially methylated; poly(4-vinylpyridine), 25% cross-linked; poly(1,2-dihydro-2,2,4-trimethylquinoline).

11. The composition as claimed in claim 10 wherein said polymeric leveler is selected from the group consisting of poly[(bis(2-chloroethyl)ether-*alt*-1,2-bis[3-(dimethylamino)propyl]urea, quaternized, and poly(diallyl dimethylammonium chloride).

12. The composition as claimed in claim 9 wherein said low molecular weight leveler is selected from the group consisting of N-containing acyclic compounds, N-containing five-membered heterocyclic compounds and N-containing six-membered heterocyclic compounds.

13. The composition as claimed in claim 12 wherein said low molecular weight leveler is selected from the group consisting of 2,5-dithiobiurea, dithiooxamide, 1-phenyl-2-thiourea, diethylenetriamine, *p*-xylenebis(tetrahydrothiophenium) chloride, 2-thiohydantoin, pseudo thiohydantoin, (R)-(-)-thiazolidine-4-carboxylic acid, 3-(2'-thiopyridinium) propyl sulfonate, 2,2'-dipyridyl disulfide, 4,4'-dipyridyl disulfide, thionicotinamide, 4-(trifluoromethyl)-2-pyrimidinethiol, 2-mercaptop-4-methylpyrimidine hydrochloride, 5-phenyl-1*H*-1,2,4-triazole-3-thiol, 5-(4'-pyridyl)-1*H*-1,2,4-triazole-3-thiol, 2-amino-6-purinethiol, 4-amino-5-(4'-pyridyl)-4*H*-1,2,4-triazole-3-thiol, diethyl heptadecyl imidazolinium ethylsulfate,

5 10 hexamethylenetetraamine, 1,3-bis(3-pyridylmethyl)-2-thiourea, 2,4-diamino-6-mercaptopurine hemisulfate, dithiouracil, 4,5-diamino-2,6-dimercaptopurine, 4,5-diamino-6-hydroxy-2-mercaptopurine hemisulfate hydrate, 4(5)-imidazoledithio-carboxylic acid, 2-mercaptop-5-benzimidazolesulfonic acid, sodium salt dihydrate, 2-thiouracil, trithio cyanuric acid, (2-pyrimidylthio) acetic acid, 7-trifluoromethyl-4-quinolinethiol, 5-carbethoxy-2-thiouracil, 1*H*-1,2,4-triazole-3-thiol, 1-phenyl-1*H*-1,2,4-triazole-5-thiol, *N,N'*-ethylene thiourea, and 2-mercaptopbenzothiazole.

14. The composition as claimed in claim 13 wherein said low molecular weight leveler is selected from the group consisting of diethylenetriamine and thionicotinamide.

15. The composition as claimed in claim 9 wherein said organic dye leveler is selected from the group consisting of Bismarck Brown Y, Chicago Sky Blue 6B and Acid Violet.

16. The composition as claimed in claim 1 further comprising a brightener/carrier molecule.

17. The composition as claimed in claim 16 wherein said brightener/carrier molecule is polymeric protein.

18. The composition as claimed in claim 1 further comprising a carrier/leveler molecule.
19. The composition as claimed in claim 18 wherein said carrier/leveler molecule is selected from the group consisting of poly[bis(2-chloroethyl)ether-alt-1,3-bis[3-(dimethylamino)propyl] urea, quaternited, and poly(melamine-co-formaldehyde).
20. The composition as claimed in claim 1 wherein the weight ratio of carrier to leveler to brightener ranges from about 0.09 to 47.6 : 0.09 to 47.6 : 0.2 to 4.7 weight/weight percent.
21. An improved method for making an acid copper electroplating bath comprising an aqueous solution of acid and copper salt, the improvement comprising adding to said bath a carrier compound; a water-soluble, mercapto-containing organic brightener compound; and a leveler compound which comprises an organic compound containing single and multiply charged centers.  
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22. The method as claimed in claim 21 wherein said carrier compound is selected from the group consisting of a polysaccharide compound, polyethylene glycol and poly(ethylene oxide).
23. The method as claimed in claim 21 wherein said polysaccharide carrier is selected from the group consisting of starch, cellulose, amylopectin and amylose.
24. The method as claimed in claim 21 wherein said water-soluble, mercapto-containing organic brightener is selected from the group consisting of *N*-methylallyl-*N'*-methylthiourea; tetramethylthiuram disulfide; ethylethylthiomethyl sulfoxide; ammonium diethyldithiocarbamate; dimethyl-2-thioxo-1,3-dithiole-4,5-dicarboxylate;  
5 3-mercaptopropanesulfonic acid sodium salt; 3-mercaptopropanesulfonic acid; bis (2-mercptoethyl) sulfide; ethylene trithio carbonate; ethanethiol; 2-mercptoethanol; monothioglycerol (1-thioglycerol); 1,2-ethanedithiol; and thiодиethanol.

25. The method as claimed in claim 24 wherein said water-soluble, mercapto-containing organic brightener is selected from the group consisting of ammonium diethyldithiocarbamate, 3-mercaptopropanesulfonic acid sodium salt, and 3-mercaptopropanesulfonic acid.
26. The method as claimed in claim 21 wherein said leveler is selected from the group consisting of polymeric levelers, low molecular weight levelers and organic dyes.
27. The method as claimed in claim 26 wherein said polymeric leveler is selected from the group consisting of polyethylenimine, 80% ethoxylated; poly (allylamine); poly (allylamine hydrochloride); polyaniline, sulfonated, 5 wt. % in water, 75 mole % sulfonated; poly[bis (2-chloroethyl)ether-*alt*-1,3-bis[3-(dimethylamino)propyl]urea, quaternized; poly[N,N'-bis(2,2,6,6-tetramethyl-4-piperidinyl)-1,6-hexanediamine-*co*-2,4-dichloro-6-morpholino-1,3,5-triazine; polyacrylamide; poly(acrylamide-*co*-diallyldimethylammonium chloride); poly(diallyldimethylammonium chloride); poly(melamine-*co*-formaldehyde), partially methylated; poly(4-vinylpyridine), 25% cross-linked; poly(1,2-dihydro-2,2,4-trimethylquinoline).  
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28. The method as claimed in claim 26 wherein said polymeric leveler is selected from the group consisting of poly[(bis (2-chloroethyl)ether-*alt*-1,3-bis [3-(dimethylamino)propyl]urea, quaternized, and poly (diallyldimethylammonium chloride).
29. The method as claimed in claim 26 wherein said low molecular weight leveler is selected from the group consisting of N-containing acyclic compounds, N-containing five-membered heterocyclic compounds and N-containing six-membered heterocyclic compounds.
30. The method as claimed in claim 26 wherein said low molecular weight leveler is selected from the group consisting of 2,5-dithiobiurea, dithiooxamide, 1-phenyl-2-thiourea, and diethylenetriamine, *p*-xylenebis(tetrahydrothiophenium) chloride, 2-thiohydantoin, pseudo thiohydantoin, (R)-(-)-thiazolidine-4-carboxylic acid, 3-(2'-thiopyridinium) propyl sulfonate, 2,2'-dipyridyl disulfide, 4,4'-dipyridyl disulfide,  
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thionicotinamide, 4-(trifluoromethyl) -2-pyrimidinethiol, 2-mercaptop-4-methylpyrimidine hydrochloride, 5-phenyl-1*H*-1,2,4-triazole-3-thiol, 5-(4'-pyridyl)-1*H*-1,2,4-triazole-3-thiol, 2-amino-6 purinethiol, 4-amino-5-(4'-pyridyl)-4*H*-1,2,4-triazole-3-thiol, diethyl heptadedecyl imidazolinium ethylsulfate, hexamethylenetetraamine, 1,3-bis(3-pyridylmethyl)-2-thiourea, 2,4-diamino-6 mercaptopyrimidine hemisulfate, dithiouracil, 4,5-diamino-2,6-dimercaptopyrimidine, 4,5-diamino-6-hydroxy-2-mercaptopyrimidine hemisulfate hydrate, 4(5)-imidazoledithio-carboxylic acid, 2-mercato-5-benzimidazolesulfonic acid, sodium salt dihydrate, 2-thiouracil, trithiocyanuric acid, (2-pyrimidylthio) acetic acid, 7-trifluoromethyl-4-quinlinethiol, 5-carbethoxy-2-thiouracil, 1*H*-1,2,4-triazole-3-thiol, 1-phenyl-1*H*-1,2,4-triazole-5-thiol, 10 *N,N'*-ethylene thiourea, and 2-mercaptop benzothiazole.

31. The method as claimed in claim 30 wherein said low molecular weight leveler is selected from the group consisting of diethylenetriamine and thionicotinamide.

32. The method as claimed in claim 26 wherein said organic dye leveler is selected from the group consisting of Bismarck Brown Y, Chicago Sky Blue 6B and Acid Violet.

33. The method as claimed in claim 21 further comprising a brightener/carrier molecule.

34. The method as claimed in claim 33 wherein said brightener/carrier molecule is polymeric protein.

35. The method as claimed in claim 21 further comprising a carrier/leveler molecule.

36. The method as claimed in claim 35 wherein said carrier/leveler molecule is selected from the group consisting of poly[bis(2-chloroethyl/ether-alt-1,3-bis[3-(dimethylamino)propyl]urea, quaternited, and poly(melamine-co-formaldehyde).

37. The method as claimed in claim 21 further adding at least one of an alkaline source compound and a chloride ion-containing compound.
38. The method as claimed in claim 21 wherein said carrier is present in a range of about 2 to 1000 parts per million, said leveler is present in a range of about 2 to 1000 parts per million and said brightener is present in a range of about 5 to 100 parts per million.
39. A method for copper plating of advanced interconnects comprising immersing said interconnects in a copper plating bath comprising an aqueous solution of an acid and a copper salt and at least one of a carrier compound; a water-soluble, mercapto-containing organic brightener compound; and a leveler compound containing single and multiply charged centers.  
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40. The method as claimed in claim 39 wherein said acid is sulfuric acid.
41. The method as claimed in claim 39 wherein said copper salt is selected from the group consisting of copper sulfate, copper acetate, copper fluoborate, cupric nitrate and copper pyrophosphate.
42. The method as claimed in claim 41 wherein said copper salt is copper sulfate.
43. The method as claimed in claim 39 wherein said carrier compound is selected from the group consisting of a polysaccharide compound, polyethylene glycol and poly (ethylene oxide).
44. The method as claimed in claim 43 wherein said polysaccharide carrier compound is selected from the group consisting of starch, cellulose, amylopectin and amylose.
45. The method as claimed in claim 39 wherein said water-soluble, mercapto-containing organic brightener is selected from the group consisting of *N*-methylallyl-

*N'*-methylthiourea; tetramethylthiuram disulfide; ethylethylthiomethyl sulfoxide; ammonium diethyldithiocarbamate; dimethyl-2-thioxo-1,3-dithiole-4,5-dicarboxylate; 3-mercaptop-1-propanesulfonic acid sodium salt; 3-mercaptop-1-propanesulfonic acid; bis (2-mercaptopethyl) sulfide; ethylene trithio carbonate; ethanethiol; 2-  
5 mercaptoethanol; monothioglycerol (1-thioglycerol); 1,2-ethanedithiol; and thiодиethanol.

46. The method as claimed in claim 45 wherein said water-soluble, mercapto-containing organic brightener is selected from the group consisting of ammonium diethyldithiocarbamate, 3-mercaptop-1-propanesulfonic acid sodium salt, and 3-mercaptop-1-propanesulfonic acid.

47. The method as claimed in claim 39 wherein said leveler is selected from the group consisting of polymeric levelers, low molecular weight levelers and organic dyes.

48. The method as claimed in claim 47 wherein said polymeric leveler is selected from the group consisting of polyethylenimine, 80% ethoxylated; poly(allylamine); poly(allylamine hydrochloride); polyaniline, sulfonated, 5 wt. % in water, 75 mole % sulfonated; poly[bis(2-chloroethyl)ether-*alt*-1,3-bis[3-(dimethylamino)propyl]urea, 5 quaternized; poly[N,N'-bis(2,2,6,6-tetramethyl-4-piperidinyl)-1,6-hexanediamine-*co*-2,4-dichloro-6-morpholino-1,3,5-triazine; polyacrylamide; poly(acrylamide-*co*-diallyldimethylammonium chloride); poly(diallyldimethylammonium chloride); poly(melamine-*co*-formaldehyde), partially methylated; poly(4-vinylpyridine), 25% cross-linked; poly(1,2-dihydro-2,2,4-trimethylquinoline).

49. The method as claimed in claim 47 wherein said polymeric leveler is selected from the group consisting of poly[(bis(2-chloroethyl)ether-*alt*-1,2-bis[3-(dimethylamino)propyl]urea, quaternized, and poly(diallyl dimethylammonium chloride).

50. The method as claimed in claim 47 wherein said low molecular weight leveler is selected from the group consisting of N-containing acyclic compounds, N-

containing five-membered heterocyclic compounds and N-containing six-membered heterocyclic compounds.

51. The method as claimed in claim 50 wherein said low molecular weight leveler is selected from the group consisting of 2,5-dithiobiurea, dithiooxamide, 1-phenyl-2-thiourea, diethylenetriamine, *p*-xylenebis(tetrahydrothiophenium) chloride, 2-thiohydantoin, pseudo thiohydantoin, (R)-(-)-thiazolidine-4-carboxylic acid, 3-(2'-thiopyridinium) propyl sulfonate, 2,2'-dipyridyl disulfide, 4,4'-dipyridyl disulfide, thionicotinamide, 4-(trifluoromethyl) -2-pyrimidinethiol, 2-mercaptop-4-methylpyrimidine hydrochloride, 5-phenyl-1 *H*-1,2,4-triazole-3-thiol, 5-(4'-pyridyl)-1 *H*-1,2,4-triazole-3-thiol, 2-amino-6-purinethiol, 4-amino-5-(4'-pyridyl)-4 *H*-1,2,4-triazole-3-thiol, diethyl heptadecyl imidazolinium ethylsulfate, 10 hexamethylenetetraamine, 1,3-bis(3-pyridylmethyl)-2-thiourea, 2,4-diamino-6-mercaptopyrimidine hemisulfate, dithiouracil, 4,5-diamino-2,6-dimercaptopyrimidine, 4,5-diamino-6-hydroxy-2-mercaptopyrimidine hemisulfate hydrate, 4(5)-imidazoledithio-carboxylic acid, 2-mercaptop-5-benzimidazolesulfonic acid, sodium salt dihydrate, 2-thiouracil, trithio cyanuric acid, (2-pyrimidylthio) acetic acid, 7-trifluoromethyl-4-quinlinethiol, 5-carbethoxy-2-thiouracil, 1 *H*-1,2,4-triazole-3-thiol, 1-phenyl-1 *H*-1,2,4-triazole-5-thiol, *N,N'*-ethylene thiourea, and 2-mercaptopbenzothiazole.

52. The method as claimed in claim 51 wherein said low molecular weight leveler is selected from the group consisting of diethylenetriamine and thionicotinamide.

53. The method as claimed in claim 47 wherein said organic dye leveler is selected from the group consisting of Bismarck Brown Y, Chicago Sky Blue 6B and Acid Violet.

54. The method as claimed in claim 39 further comprising a brightener/carrier molecule.

55. The method as claimed in claim 54 wherein said brightener/carrier molecule is polymeric protein.

56. The method as claimed in claim 39 further comprising a carrier/leveler molecule.
57. The method as claimed in claim 56 wherein said carrier/leveler molecule is selected from the group consisting of poly[bis(2-chloroethyl)ether-alt-1,3-bis[3-(dimethylamino)propyl] urea, quaternized, and poly(melamine-co-formaldehyde).
58. The method as claimed in claim 39 wherein said carrier is present in the composition in an amount ranging from about 2 to about 1000 parts per million parts water.
59. The method as claimed in claim 39 wherein said leveler is present in the composition in an amount ranging from about 2 to about 1000 parts per million parts water.
60. The method as claimed in claim 39 wherein said brightener is present in the composition in an amount ranging from about 5 to about 100 parts per million parts water.
61. The method as claimed in claim 39 wherein said carrier/brightener is present in an amount ranging from about 5 to about 1000 parts per million parts water and said carrier/leveler is present in an amount ranging from about 2 to about 1000 parts per million parts water.
62. The method as claimed in claim 39 wherein said compounds are added either individually or as combinations to said aqueous solution.
63. The method as claimed in claim 39 wherein a current between 3 mA/cm<sup>2</sup> and 40 mA/cm<sup>2</sup> is applied to said solution.

64. The method as claimed in claim 63 wherein the wave form of said current is selected from the group consisting of direct current, pulse current and pulse reverse current.